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Modeling of the radiation-induced microstructural evolution in ionic crystals

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Abstract

Results of experimental and theoretical investigations are presented on heavily irradiated natural and synthetic NaCl crystals in the temperature range where anion defects are mobile. They give a strong evidence for the formation of vacancy voids, which cannot be explained by the Jain–Lidiard model used up to date for description of metal colloids and dislocation loops formed in ionic crystals during earlier stages of irradiation. We consider an additional set of reactions between experimentally observed extended defects (metal colloids, gas bubbles and voids) and point defects. The latter include F and H centers that are the primary defects produced by irradiation, and cation vacancies (with a trapped hole) that are secondary defects, produced in the process of dislocation climb due to absorption of extra H centers. We show that highly overpressurized bubbles of fluid halogen are strongly biased for absorption of H centers, which makes them grow via punching out interstitial dislocation loops. The loops grow and produce cation vacancies that are subsequently trapped at the incoherent colloids together with extra F centers giving rise to the colloid–void transition. Elastic interaction between extended defects and point defects is shown to play a major role, since it determines the bias factors of extended defects, which is a major driving force of the microstructural evolution under irradiation. A quantitative comparison of the new model for radiation damage in NaCl with experimental data is presented. Mean sizes and volume fractions of all types of observed defects are calculated. It is shown that voids formed due to agglomeration of F centers and cation vacancies can grow to the dimensions exceeding the mean distance between colloids and bubbles, eventually absorbing them, hence, bringing the halogen gas and metal to a back reaction. Impurities play a major role in the void development with increasing irradiation dose, which strongly affects the radiation stability of NaCl.

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Keywords: Radiation damage; Alkali halides; Microstructure evolution; Vacancy voids

1. Introduction

Irradiation of ionic crystals causes the displacements of lattice ions and the formation of primary defects in the form of vacancies and interstitials. Stabilization of primary point defects in

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ionic crystals, however, differs from that in metals because primary point defects seldom are produced in exactly stoichiometric proportions, as a result, at high temperatures, when these defects are mobile, secondary defects and extended defect structures arise which can be quite distinct from those formed in monoatomic solids. A well known example of this effect occurs in the alkali halides, where the principal radiation damage consists of clusters of halogen molecules and of complementary inclusions of alkali metal (*colloids*) formed by agglomerating F centers [1]. There is also evidence that clusters of halogen molecules are in the form of *bubbles of fluid halogen*. Hobbs et al. [2] showed that irradiation at low temperatures (where vacancy defects were quite immobile) led to the formation of *perfect* interstitial dislocation loops. Such perfect loops require both interstitial halogen and interstitial alkali metal: but all previous work showed that ionization damages only the halide sub-lattice. The accepted explanation was that a cluster of some small number of halogen molecules formed an interstitial platelet, i.e. a faulted loop, which then "unfaulted" at a certain size to give the observed perfect loop structures and a corresponding number of dispersed halogen molecular centers [1]. In 1977, Jain and Lidiard [3] have formulated a model, according to which, *the dislocation bias* for H centers was the driving force for the colloid growth in alkali halides as it was for the *void growth in metals* under irradiation. Until recently, the Jain–Lidiard model was considered to work well providing a qualitative explanation of the radiation damage in alkali halides.

From our results [4–6] obtained for NaCl after irradiation up to 150 Grad (about 30 displacements per atom), it follows that large *vacancy voids* (up to hundreds of nm in size) form in NaCl samples (with particular dopants), which cannot be, in principle, explained by the conventional theory. In the next section, we present a new model of radiation damage in alkali halides.

2. New insight in the microstructure evolution in alkali halides

We will again use an analogy with radiation damage in metals. The elastic interaction between inclusions or cavities (which can be voids, gas bubbles or solid precipitates) and point defects (PD) was shown to result in the inclusion bias for absorption of PD, which depends on the inclusion size and the normal stress at its boundary [7]. The difference between the bias factors of extended defects (ED) of different kinds or sizes is the main driving force of the microstructural evolution under irradiation.

2.1. The role of halogen bubbles

It follows from the above mentioned results [7] that highly overpressurized halogen bubbles ($P \gg 2\gamma/R$, where $2\gamma/R$ is the surface tension, and P the gas pressure) can be strongly biased for H absorption, which can be *a primary driving force* for the separation of the H and F centers into bubbles and metal colloids. When several H centers come together they combine to form a halogen bubble which "digs its own hole" in the lattice by punching out a perfect self-interstitial loop (SIA-loop). This process is exactly analogous to the loop punching from helium bubbles in metals that was predicted in 1959 [8] and confirmed experimentally ever since [9]. It is more favorable energetically than the production of a number of dispersed molecule centers as it was assumed in the Jain–Lidiard model. The threshold pressure for the loop punching is inversely proportional to the bubble radius [8]. It means that small halogen bubbles have a higher bias for H centers than that of dislocations, and they can transform the difference between incoming H and F centers into perfect SIA-loops. Both of these defects can be observed experimentally.

2.2. Vacancy void formation

When an H center approaches dislocation, it forms a stoichiometric di-interstitial (needed for the dislocation climb) *leaving behind a cation vacancy* (*CV*) (with a trapped hole) that is even more mobile than the F center. Coherent colloids are transparent for CV, but as soon as the colloids loose coherency, they start to trap CV that would react with incoming F centers to produce stoichiometric di-vacancies that would subsequently

convert incoherent colloids into vacancy voids attached to colloids. Voids grow faster than colloids, since they have no misfit stress and so have smaller bias to H centers, δ_V, as compared to that of coherent colloids, δ_C:

$$\delta_V = \alpha_{im} b/R_V, \quad \delta_C = \alpha_{im} b/R_C + \alpha_\mu(\sigma_\varepsilon/\mu^2),$$
$$\sigma_\varepsilon = 8\mu_C \varepsilon/(1 + 2\mu_C/\mu),$$

where μ_C is the colloid shear modulus, and ε the misfit that determines also a threshold colloid radius for the loss of coherency, $R_C^{th} \approx \mu b/\sigma_\varepsilon$. Dimensionless constants, α, are the coefficients corresponding to different modes of elastic interaction between PD and ED [7].

Fig. 1 illustrates the radiation-induced reactions between PD and ED based on the present model. Primary PD, namely, H and F centers, separate ultimately into bubbles, dislocations and metal colloids, which results in production of the secondary PD (cation vacancies) and ED (interstitial loops and vacancy voids).

A quantitative comparison of the model predictions with experimental data is presented in the next section.

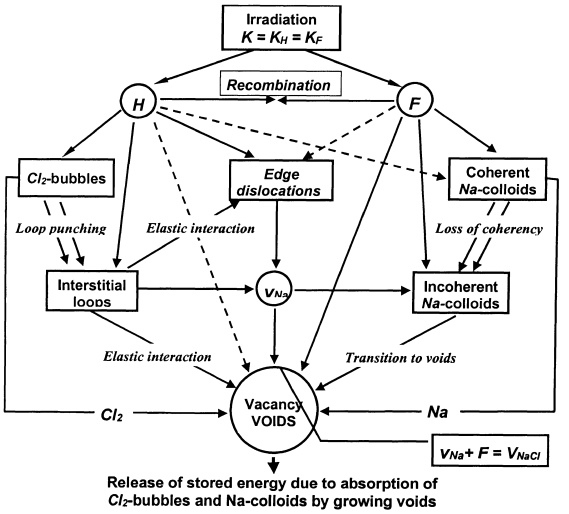

Fig. 1. Diagram of radiation-induced reactions between point defects (H and F centers, and cation vacancies) and extended defects (bubbles, dislocations and colloids) resulting in the void formation.

3. Experimental observations

The natural and doped NaCl crystals have been irradiated with 1.35 MeV electrons up to doses of 150 Grad (about 30 dpa) at temperatures between 50°C and 150°C. Scanning electron microscopy (SEM) in combination with differential scanning calorimetry (DSC) and electron spin resonance (ESR) were used to study the void production. The concentration of the metallic Na was deduced from measurements of the latent heat of melting of metallic Na in combination with ESR.

Formation of large voids (above 100 nm in diameter) correlates with an eventual destruction of the samples under heavy irradiation or heating without any observable loss of the specimen weight, which confirms that the cavities are vacancy voids rather than gas-filled bubbles. Impurities strongly affect the void development as well as the accumulation of metallic Na.

4. Comparison of the model predictions with experimental data

Based on the model, a complete set of the rate equations for PD and growth rates for ED was derived, which is described in detail elsewhere [11]. An asymptotic (in time of irradiation) solution to these equations was obtained in the temperature range ($0.3T_m < T < T^{th}$), in which both anion and cation PD are mobile but thermal evaporation of PD from ED can be neglected. In this region, the growth or shrinkage rates of different kinds of ED and their sizes are determined by the difference between the incoming fluxes of radiation produced PD, which is determined by several material constants presented in Table 1. We have used experimentally observed values for the mean dislocation density, ρ, and the void nucleation rate, K_{Void}, as the only input microstructural parameters (see Table 1). The mean sizes and number densities of colloids and bubbles as well as the mean size of voids have been calculated as a function of irradiation dose at the stage after the nucleation stage of colloids. Under this condition, the colloid number density is independent of the initial conditions and is deter-

Table 1
Principal material and irradiation parameters used for the calculations in the present paper

Parameter	Value
Dislocation bias, δ_d	0.5
$\delta_{eff} = \delta_d - \alpha_\mu(\sigma_\varepsilon/\mu)^2$	0.1
Image interaction constant, α^{im}	0.1
Modulus interaction constant, α^μ	100
Shear modulus, μ (GPa)	15
Colloid shear modulus, μ_C (GPa)	3.3
Colloid misfit, ε	0.05
Irradiation temperature, T (°C)	100
Dose rate, K, Mrad h^{-1} (dpa s^{-1})	120 (6×10^{-6})
RIC upper temperature , T^{th} (K), °C	220
Maximum dose, Grad (dpa)	150 (30)
F–H recombination constant, (m^{-2})	10^{20}
Dislocation density, ρ (m^{-2})	1×10^{14}–5×10^{14}
Void nucleation rate, K_{Void} (dpa^{-1} m^{-3})	10^{18}–10^{19}

mined by the radiation-induced coarsening (RIC) mechanism, which was originally proposed for voids in irradiated metals [12].

Fig. 2(a) shows the measured dose dependence of the latent heat of melting (LHM) of Na (which is proportional to the total content of metallic Na) in samples doped with different impurities along with the theoretical curves corresponding to different dislocation densities. Fig. 2(b)–(d) show the measured and calculated dependencies of void parameters on LHM. The mean sizes and number densities of colloids and bubbles were not measured, while their maximum theoretical values were found to be about 6 nm and 10^{23} m^{-3} for colloids, and 60 nm and 5×10^{19} m^{-3} for voids, respectively. For doses higher than 50 Grad, the void dimensions exceed the mean distance between colloids and bubbles, which makes possible the capture of the latter by growing voids that would eventually bring the halogen gas and metal to a back reaction. Thus, the present model offers a natural explanation not only for the void formation, but also for the observed release of stored energy with increasing irradiation dose.

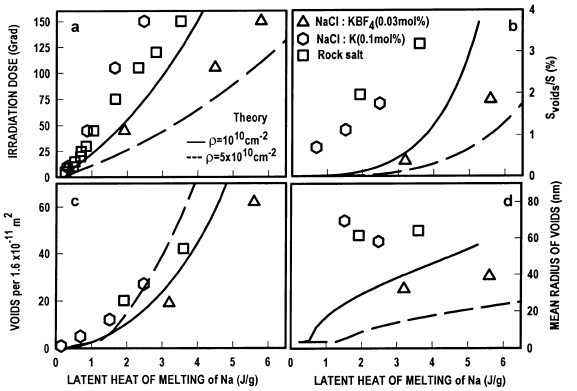

Fig. 2. Measured and calculated dependence of LHM of metallic Na on irradiation dose (a), and the void mean parameters against LHM for different dopants and dislocation densities, ρ. Symbols – experimental data, curves – theory.

Acknowledgements

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